

PATENT SPECIFICATION

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A process for the production of polyhydric alcohol mixtures by degradative hydrogenation of sugars.

COMPLETE SPECIFICATION

We, UDIC SOCIETE ANONYME of Rue de Lausanne 6, Vevey/Vaud, Switzerland, a Swiss company, do hereby declare the invention, for which we pray that a patent may 5 be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

In the hydrolysis of vegetable materials, such as softwoods, hardwoods, cotton stalks, 10 bagasse, and so forth, with mineral acids, sugar mixtures of different compositions depending upon the nature of the raw material may be obtained. For instance mixtures of the following percentage composition may be obtained from softwoods:

glucose 82.5%; mannose 6.4%; xylose 5.8%; polymeric sugars 3%; arabinose 1.2%; galactose 1.1%;

whereas mixtures of roughly the following 20 compositions may be obtained from beech-wood:

glucose 87%; mannose 5.0%; polymeric sugars 4.0%; xylose 3.2%; galactose 0.5%.

If it is desired to convert the sugar solutions thus obtained into polyhydroxyl compounds by degradative hydrogenation it has been hitherto necessary first to perform costly purifying processes to provide limpid 25 sugar solutions free from salts, acids, and degradation products, because the sugar solutions had to be thus purified before they could be submitted to degradative catalytic hydrogenation.

The present invention is based on the discovery that by maintaining the pH value 30 of the sugar solutions intended for degradative catalytic hydrogenation at a steady level of at least 8, preferably 9 to 10, the degradative hydrogenation of the crude dark brown hydrolysed mixture was successfully accomplished, at temperatures starting as low as 100° and rising to a maximum of 160°C. in the presence of hydrogenation catalysts for 45 example finely-divided metallic catalysts such

as nickel precipitated on carrier materials, such as active carbon, in such manner that the quantity of resultant lower hydroxyl compounds, such as ethylene glycol, but also that of the higher hydroxyl compounds, such 50 as mannitol is reduced in favour of the glycerine components in such manner that, on the one hand the viscosity of the solution is not unduly diminished and, on the other hand the risk of crystallisation of the difficultly soluble mannitol is avoided.

There is provided by the present invention a process for hydrogenating a crude solution 55 of sugars obtained from the mineral-acid hydrolysis of cellulose and/or hemicellulose present in cellulosic material to convert said sugars to polyhydric alcohols having a less number of carbon atoms than said sugars which process includes the steps of catalytically hydrogenating said crude solution of 60 sugars at a temperature of from 100 to 160°C. wherein said crude solution is maintained at a pH of at least 8 throughout the hydrogenation.

It is preferred to react mixtures of sugars 70 obtained by the hydrolysis in which the polymeric sugars, after the conventional after-hydrolysis, have been degraded into monomeric sugars, e.g. monomeric pentoses and hexoses, together with the residual acid 75 which remains after the mineral acid required for hydrolysis has been removed by distillation and which amounts in order of magnitude to about 3%.

Alkali may be added initially to the solution to establish the required pH, and to maintain the pH value at a constant level during the degradative hydrogenation process alkali such as lime water, magnesia, carbonate of soda, trimethylamine, and the like may be added continuously or continually. The reagents for maintaining the necessary pH value are introduced into the reaction mixture, when during the reaction the pH value falls, by metering pumps, pre- 80
85
90

ferably in the form of dilute aqueous solutions or suspensions. However, especially in the discontinuous process suitable substances of only limited solubility in water, such as calcium carbonate and magnesia may be added to the material before hydrogenation.

Preferred catalysts are active nickel catalysts precipitated on to carrier substances, such as active carbon, or kieselguhr.

With reference to the necessary apparatus, degradative hydrogenation requires no special plant. Any conventional hydrogenation apparatus is applicable, and also apparatus consisting of iron which is an inexpensive material, because the process of the invention is performed exclusively in the alkaline range of pH values and acid attack on the material cannot therefore occur.

The proposed process can be applied equally well to the hydrogenation of crude acid-hydrolysed products obtained from the hydrolysis in which both the readily and difficultly hydrolysable carbohydrate portions of the cellulosic material containing hemicellulose and cellulose are hydrolysed together, and to the hydrogenation of crude products obtained from each step of the hydrolysis in which said readily and difficultly hydrolysable carbohydrate portions are hydrolysed in separate steps.

The alcohol mixtures thus obtained, which may be further purified by conventional methods, for instance by ion exchange reactions, are *inter alia* excellent moisture-retaining media and anti-freeze agents in water.

EXAMPLE 1

A nickel catalyst precipitated on active carbon (ratio of A-carbon to nickel 10:1), containing 1.6% by weight of nickel in relation to the quantity of sugar, is suspended in a 45% aqueous sugar solution obtained by the acid hydrolysis of hardwood and having the following composition:

45	xylene	31.7%
	mannose	29.0%
	glucose	27.9%
	polymeric sugar	1.5%
	galactose	5.3%
50	arabinose	4.6%

which was adjusted by the addition of a 1 10N caustic soda solution to a pH of 9. Degradative hydrogenation is first performed for 5 hours at 100°C. and 60 atmospheres hydrogen pressure and then continued for another 3 hours at 130°, the necessary quantities of an 0.05% solution of carbonate of soda being added from time to time to prevent the pH value in the course of the reaction from falling below the adjusted pH. The catalyst is separated from the reaction mixture which has been formed and the water is distilled off under atmospheric pressure. In the subsequent vacuum distillation there are obtained, in the first fraction at 85

to 125°C. and 13-15 mm Hg. pressure a mixture of dihydric alcohols, namely about 7% ethylene- and 8% propylene glycol, in relation to the total quantity of polyalcohol, and in a second fraction in a boiling interval of 125 to 185°C. and 13 to 15 mm. Hg. an alcohol mixture consisting mainly of 54% glycerine and 9% methyl glycerine. The distillation residue of 22% is composed of 14% sorbitol, 2% mannitol, 4% xylitol, 1% erythritol and 1% other polyhydric alcohols.

EXAMPLE 2

In a 46% aqueous sugar solution obtained, without separation of the easily and difficultly hydrolysable carbohydrate portions, by the acid hydrolysis of beechwood, and having the following percentage by weight composition:

glucose	46.1%
xylene	44.6%
mannose	3.7%
polymeric sugar	2.0%
galactose	1.8%

a catalyst consisting of reduced nickel precipitated on kieselguhr (proportion of kieselguhr to nickel 10:1) was suspended in such quantities that 1.7% nickel was available for the entire quantity of sugar. A pH value of 9.3 is adjusted with caustic soda and maintained at this level during the reaction with 95 lime water. Degradative hydrogenation is performed for five hours with a hydrogen pressure of 66 atmospheres at 105° and then continued to completion for three hours at 130°C. The catalyst is separated from the reaction mixture which has been formed and the water is distilled off under atmospheric pressure. In the subsequent vacuum distillation there are obtained in the first fraction at 85 to 125°C. and 13 to 15 mm. Hg. pressure, a mixture of dihydric alcohols, namely about 4% ethylene- and 6% propylene glycol, in relation to the total quantity of polyalcohol, and in a second fraction in a boiling interval of 125 to 185°C. and 13 to 110 15 mm. Hg. pressure an alcohol mixture consisting mainly of glycerine and 5% methyl glycerine. The distillation residue of 11% is composed of 7% sorbitol, 1% mannitol, 2% xylitol, 0.5% erythritol and 0.5% other polyalcohols.

WHAT WE CLAIM IS:

1. A process for hydrogenating a crude solution of sugars obtained from the mineral-acid hydrolysis of cellulose and/or hemicellulose present in cellulosic material to convert said sugars to polyhydric alcohols having a less number of carbon atoms than said sugars which process includes the steps of catalytically hydrogenating said crude solution of sugars at a temperature of from 100 to 160°C. wherein said crude solution is maintained at a pH of at least 8 throughout the hydrogenation.

2. A process according to claim 1 wherein

said solution is maintained at a pH of between 9 and 10 throughout said hydrogenation.

3. A process according to claim 1 or 5 claim 2 wherein alkali is added initially to said solution to establish the pH thereof which thereafter, during the hydrogenation, is maintained by the further addition continually or continuously, of alkali.
- 10 4. A process according to claim 3 wherein said alkali is sodium hydroxide, calcium hydroxide, sodium carbonate, calcium carbonate, magnesia or trimethylamine.
- 15 5. A process according to any of the preceding claims wherein the catalyst employed is finely-divided nickel.
- 20 6. A process according to claim 5 wherein said finely-divided nickel is deposited on active carbon or kieselguhr.
7. A process according to any of the pre-

ceding claims wherein said crude solution of sugars has been distilled to remove mineral acid therefrom.

8. A process for the production, by hydrogenation of a sugar, of a polyhydric alcohol 25 having a less number of carbon atoms than said sugar substantially as hereinbefore described with reference to either of Examples 1 and 2.
9. Polyhydric alcohols when produced by 30 the process of any of the preceding claims.

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